Superconductivity of layered compounds C_6K and C_4K

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The discovery of a superconducting transition at $T \simeq 1.5$ K in a layered compound consisting of graphite and potassium C_6K is reported. The compound C_4K exhibits a diffuse superconducting transition which begins at $T \simeq 5.5$ K.

A layered graphite compound (LGC) is an alternating sequence of hexagonal graphite lattices and monomolecular or monatomic reagent layers. Such a structure accounts for the presence in layered graphite compounds of several new physical properties and for their strong anisotropy. At present, we know that among these compounds there are two-component superconducting compounds $C_8M(M = K,Rb,Cs)$ and three-component superconducting compounds C_x, KHg, C_xKTl, and $C_x KH_y$ (Refs. 1 and 2). Since the superconducting properties of these compounds have a strong anisotropy, these compounds are promising candidates for a search for quasi-two-dimensional superconductors. Furthermore, the components of C_8M compounds are normal and the superconductivity of LGC is far from being understood. These circumstances account for the considerable interest in studying the superconductivity of these compounds.

The C_8K compound belongs to the one-step layered graphite compounds (alternation of the metal atoms with graphite every other layer is called a one-step alternation and alternation of the metal atoms with graphite every two layers is called a two-step alternation, etc.) and corresponds to the maximum saturation of graphite with potassium when the compound is synthesized by the conventional gas-phase method.[1] The critical temperature of the superconducting transition (T_c) of this compound is in the range[1-3] 0.12–0.18 K. The critical temperature remains constant as the potassium concentration is reduced to a level corresponding to that of $C_{14.7}K$. No superconducting transition is observed (more exactly, $T_c <$ mK) upon further reduction of the metal.[4] It is therefore important to synthesize a LGC with a higher potassium concentration and to determine whether T_c of this compound varies.

The reaction through which potassium is introduced into graphite is known to be accompanied by a marked reduction in volume (20–50%). A synthesis of layered graphite compounds by a high-pressure method has been suggested. The basic possibility of such a synthesis was demonstrated for the first time in Ref. 5. The study of superconductivity of such compounds in Ref. 6 led to the following basic results. First, T_c of the C_8K compound, which was synthesized by the method used in Ref. 5, is 0.13 K, consistent with the data found in the literature. Secondly, the samples with an elevated potassium content exhibit a diffuse superconducting transition, which begins at $\simeq$1.3 K and ends at 0.13 K. Despite the fact that these data inspired a certain optimism, the following important questions remained unclear: The cause of the diffuse transition, the composition of the sample after it has been synthesized, the stability of the sample, and the fact that not all samples exhibit a superconducting transition.

In the present letter we address the following problems. 1) Synthesis of LGC samples with an elevated potassium content by the high-pressure method, i.e., synthesis of C_xK, where $x < 8$. Determination of the conditions under which they are stable. 2) Determination of the composition of the samples—the synthesis products—by the direct-volume method. 3) Measurement of T_c of the synthesized samples.

The LGC samples with potassium were synthesized in a high-pressure "cylinder-and-piston" apparatus under conditions of quasi-hydrostatic pressure of up to 20 kbar and at a temperature of up to 573 K with a simultaneous detectoin of the processes involving a change in volume. By measuring the pressure (P) as a function of the displacement of the piston (L) proportional to the change in the sample's volume we were able to calculate the composition of the samples. The amount of metal implanted into the graphite was calculated from the difference between the change in the sample's volume, $\Delta V_{\rm exp}$, and the change in the volume, ΔV, corresponding to the increase in the volume of the intercalated graphite compared with the original graphite. The change in the sample's volume $\Delta V_{\rm exp}$ was determined by a computer extrapolation of the corresponding (before and after the implanting reaction) parts of the $P(L)$ curve to $P = 0$. The value of ΔV was calculated as $\Delta V = (d_i/d_j - 1)V_{\rm gr}$, where $V_{\rm gr}$ is the volume of the original graphite, $d_j = 3.35$ Å is the spacing between the planes in the original graphite, and $d_i = 5.34$ Å is the spacing between the planes in the intercalated graphite. The value of d_i was assumed to be independent of the concentration of the potassium atoms in the layer.[7] We have found from an analysis of the $P(L)$ curves and some calculations that the composition of the synthesized samples is close to that of

C_6K and C_4K, depending on the ratio of the quantity of the original components and the experimental conditions. The removal of pressure leads to a decomposition of the synthesized LGC samples into compounds less rich in potassium and into pure potassium. To stabilize the high-pressure phases, we have therefore hardened in liquid nitrogen all synthesized samples directly under load. The samples were subsequently stored in liquid nitrogen.

The temperature dependence of the magnetic susceptibility $\chi(T)$ of the synthesized samples was studied by an inductive contact-free method in an apparatus in which the He^3 vapor was pumped off, at temperatures in the range 0.6–20 K. The temperature was measured with a "SPEER" carbon thermometer, which was calibrated against the He^3 vapor pressure at $T \leqslant 1.5$ K and against the He^4 vapor pressure at $T \leqslant 4.2$ K, and with a semiconductor thermometer above 4.2 K. Under no circumstances were the test samples heated above the liquid-nitrogen temperature. Before carrying out the measurements, the sample was inserted into one of the two oppositely wound coils which, along with the thermometers, was installed in a low-temperature chamber. The modulating coil was placed into the external vessel with He^4. The frequency of the modulating field was 111 Hz and its amplitude was $\simeq 0.1$ Hz.

Figure 1a is a plot of a typical $\chi(T)$ curve for the C_6K sample. At $T \simeq 1.5$ K we see a sharp jump in the susceptibility, which can be attributed to the transition of the sample to the superconducting state. The width of the transition region, defined as 90% of the total change in the susceptibility, is $\simeq 0.2$ K and in one of the samples it is less than 0.1 K. The critical temperature T_c, determined from the midpoint of the jump on the $\chi(T)$ curve, is in the range 1.45–1.55 K for the seven samples studied by us. In the other four samples, whose composition is close to that of C_4K, a change in $\chi(T)$ begins to be noticeable at $\simeq 5.5$ K and is seen over the entire temperature interval (Fig. 1b). After a short warming of the samples to 300 K, the superconducting transition becomes diffuse. In the case of longer warming periods, the transition decreases in magnitude or vanishes entirely. After storing the synthesized samples in

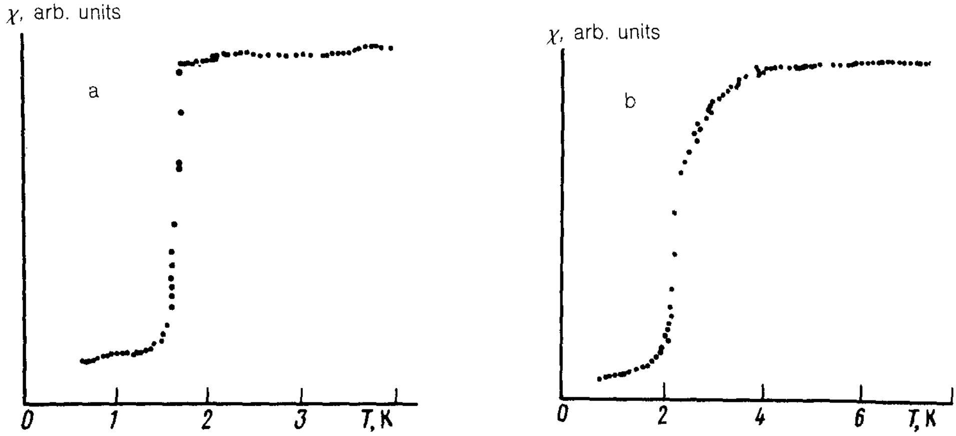

FIG. 1. Temperature dependence of the magnetic susceptibility $\chi(T)$. a—C_6K sample; b—C_4K sample.

liquid nitrogen for one year, no changes in the superconducting transition in them were observed.

In our experiments we were not able to achieve a sharp transition to the superconducting state in C_4K samples. A diffuse transition is apparently a consequence of the local stress and the presence of lattice defects in the samples or the inhomogeneity of the composition of these samples. The last factor in turn may reflect incomplete synthesis of the C_4K phase because of degraded experimental conditions (temperature, pressure) or insufficient stability of C_4K even at 77 K. We intend to pursue the study of this problem.

As a result of our experiments, we have thus been able to synthesize several sets of LGC samples with a composition close to C_6K and C_4K which were hardened under load in liquid nitrogen. In all synthesized samples we observed a transition to the superconducting state at a critical temperature considerably higher than that of C_8K, indicating that T_c depends strongly on the concentration of metal in the LGC with potassium.

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